Near-junction Phenomena in Cu(In,Ga)Se$_2$ Solar Cells

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ABSTRACT

This paper summarizes recent advances at the University of Illinois on understanding fundamental limitations to device performances in CIGS solar cells. Here, we present two primary results, (1) a model of the nature of CIGS heterojunctions, and (2) the results of AMPS computer simulations on graded-junction absorber layers. A model for surface charge formation and defect incorporation leading to an inverted surface in the absence of a segregated second phase is presented. The results suggest that the CIGS surface orientation could be important for high-performance heterojunctions. AMPS modeling shows that a dip in the conduction band beyond the depletion region results in a loss of red photoresponse. The maximum acceptable penetration depth of the S is directly related to the doping level in the junction region.

1. Introduction

Photovoltaic devices based on CuInSe$_2$ have the highest performance of any thin film device. However, many questions remain to be answered concerning their operation. Understanding the nature of the heterojunction and the composition and electronic properties of the near surface region and how these affect device performances are crucial.

2. Surface States and the Heterojunction

Recent studies by this group have shown[1,2] that the non-polar (220) surface of CIGS spontaneously decomposes into charged (112)-type facets. This is remarkable when one considers that the Madelung energy arguments of classical solid-state physics work against such a phenomenon. Clearly, a surface modification must occur such that the surface charge is eliminated. This suggests that significant chemical differences exist on or near the two polar surfaces relative to a bulk layer. To explore this issue in greater depth, we have taken advantage of our ability to control surface orientation through epitaxy. We have grown both the Se and the metal-terminated (112) polar CIGS surfaces and have studied air-exposed surfaces by angle-resolved X-ray photoelectron spectroscopy (XPS). These are the surfaces typically used to fabricate solar cells. Both show a 1-3 monolayer thick oxide of the group III elements and devoid of Cu. However, Cu is found in the underlying monolayers of material. No differences in the valence band spectra were found for the two surfaces. In addition, atomic-force microscopy measurements showed very similar surface morphologies for the two surfaces, although the Se-terminated surface contains a much higher density of surface steps. The surface structure suggests that only one type of atomic step is present on these surfaces, probably the Se-terminated step. Experiments are currently underway to study Se-capped (non-air-exposed) surfaces by XPS and to perform atomic-resolution measurements of the surface reconstruction by low-energy electron diffraction and scanning tunneling microscopy. Additional experiments are being conducted with L. Brillson at the Ohio State University characterizing the near surface depth dependence of cathodoluminescence and photoluminescence.

From these and previous results, we conclude that the surface of CIGS grows by rapid nucleation and gradual growth of Se terminated steps across Se-terminated surface terraces on a surface such as the (220). This causes the Se-terminated terraces to be rough and leaves the metal-terminated terraces, on which nucleation is slow, relatively smooth. Similarly, on polar surfaces the surface grows by Se-terminated step motion. Step density depends upon the rate of nucleation of new terraces. Thus, on the Se-terminated surface the step density is much higher than on the metal-terminated surface.

Based on the Madelung argument, we anticipate that a Se-terminated surface must transfer electrons to the metal-terminated face to provide surface charge neutrality. This transfer will result in point defect generation or surface reconstruction. This can be accomplished with a modest number of surface atomic defects (antisites or vacancies) without recourse to a full surface phase. We further note that incorporation of an In on a Cu site (In$_{Cu}$) antisite defect into a step edge would tend to promote the formation of Cu vacancies on adjacent surface sites to form neutral defect clusters. The formation of vacancies would retard surface step growth locally. This may account in part for the surface morphology observed.

3. Device Analysis and Modeling

In addition to the surface growth studies on epitaxial layers, we have conducted experimental characterization and modeling of samples distributed under the CIS Thin Film Partnership Team. In particular, we analyzed a solar cell layer from Siemens Solar Industries and modeled the resulting device performance using the AMPS computer code. Based on composition depth profiles obtained by secondary-ion mass spectrometry and Auger electron spectroscopy by us and at NREL, we estimated the band edge positions as a function of depth in the absorber layer (see Fig 1). This data was used to implement a model of the corresponding solar cell using the AMPS computer code. The results were compared with experimental data giving spectral response as a function of bias voltage and current/voltage characteristic as a function of temperature. The spectral response comparison is shown in Figure 2. The spectral response data fits well, although the current
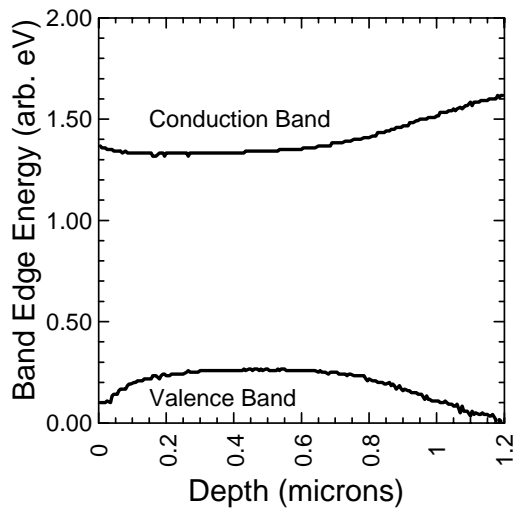
Figure 1. Estimated conduction and valence band edges as a function of depth through the absorber layer based on AES and SIMS depth profiles.
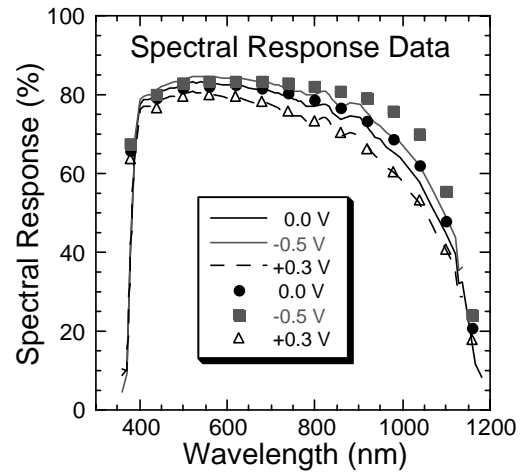

Figure 2: Spectral response data (lines) on a Siemens Solar Industries solar cell produced for the Thin Film Partnership "round robin" study for three bias voltages. Points indicate the AMPS fit results.

voltage curves are less adequate for calculations to date. The preliminary conclusions of the fit are as follows.

First, the general shape of the bias-dependent spectral response shows a poor response to red photons. The change in valence band energy due to a surface sulfur treatment is most critical to fitting this behavior. The implementation of the band edges shown in Figure 1, results in this response for expected hole densities. A shallower sulfur distribution should have resulted in a much-improved red response.

Second, the bias-dependence of the spectral response is most strongly connected to the defect density in the device. The exact level of defect density probably also affects the non-ideality of the device. The cells being modeled here appear to have a second junction in series with the collecting junction and some series resistance, which makes fitting more difficult. More specific conclusions will be possible when a more complete data fit is achieved.

4. Conclusions

Experiments indicate that the surface of CIGS strongly prefers polar (112) orientations. A surface energy argument indicates that the surfaces must reconstruct or accumulate point defects to balance their surface charges. Thus, surface inversion may not require a 135 phase. Device modeling of near surface sulfur gradients points to the importance of careful control of the sulfur penetration depth.

REFERENCES

[1] D. Liao and A. Rockett, "(220)-Oriented Cu(In,Ga)Se$_2$ -- Evidence That It May Improve Solar Cell Performance," in Proceedings of 28th IEEE PV Specialists Conference, September 17-19, 2000, Anchorage, AK, in press.

[2] D. Liao and A. Rockett, J. Appl. Phys., submitted.